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Gentlemen:

Attached is the First Quarterly Report for NASW-1415, covering work done during June, July and August, 1966.

Bernard Grushkin
Principal Investigator

BG:md

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Synthesis of Linear, Double Chain, Ladder Polymers from Substituted Tetraphosphonitriles

Quarterly Progress Report Covering the Period
June, July and August, 1966

By

Bernard Grushkin, Principal Investigator
Robert M. Murch

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ABSTRACT

12222

A mixture of $[CH_3PN(NH_2)]_{3,4}$ has been prepared. The amide as well as the chlorocompound is hydrolytically unstable. The amide, when heated above 150°C eliminates ammonia and when heated above 400°C eliminates ethylene.

Large amounts of β-trans-$[\phi PNCl]_4$ and β-trans-$[\phi PNNH_2]_4$ have been prepared. Ammonia elimination from the tetrakisamide begins at about 200°C.. Elimination of ammonia at the lower temperatures, 209° to 230°, results in the formation of low molecular weight soluble polymers with a degree of polymerization primarily of 2 to 5 as well as a chloroform insoluble polymer.

Author

RESULTS AND DISCUSSION

I. Preparation of $[CH_3PN(NH_2)]_{3,4}$

Non-geminal methylaminophosphonitriles can be prepared by the following sequence of reactions.[1]

1. $CH_3PCl_2 + Cl_2 \rightarrow CH_3PCl_4$

2. $XCH_3PCl_4 + XNH_4Cl \rightarrow [CH_3PNCl]_x + 4XHCl$

3. $[CH_3PNCl]_x + NH_{3(ex)} \rightarrow [CH_3PN(NH_2)]_x + NH_4Cl$

The yield of methylphosphonitrile obtained from reaction (2) is poor, approximately 20-30 percent. Yields of pure product are further reduced during the work-up since $[CH_3PNCl]$ appears to be hydrolytically unstable. For this reason the crude product was reacted with anhydrous ammonia to form the amide. The amide was separated from by-product ammonium chloride by extraction with acetonitrile. An infrared spectrum of the crude amide is shown in Figure 1. The weak absorption at 2650 $cm.^{-1}$ (due to POH) indicates that some hydrolysis has occurred.

Thermal deammoniation of the amide takes place above 150°C. and is essentially complete at about 400°C.. At temperatures above 400°C., degradation occurs. The principal volatile degradation product is ethylene which was identified by mass spectroscopy.

Based on the above results, namely (1) hydrolytic instability of both $[CH_3PNCl]_4$ and $[CH_3PN(NH_2)]_4$ which would make isolating and characterizing isomers of $[CH_3PNCl]_4$ exceedingly difficult and, (2) the thermal instability of polymeric methyl phosphonitrile, we have decided at this time to suspend further work on this system.

II. Polymers from β-trans-$[\phi PNCl]_4$

β-trans-$[\phi PNCl]_4$, m.p. 248-255°, was isolated in 40 to 45 percent yields from the reaction of ϕPCl_4 with NH_4Cl in the absence of solvent.[2] The reaction was carried out at 150°C. and was complete in 48 hours.

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1. Second Annual Report NASw-924
2. I.I. Bezman, German Patent 1,171,915 June 11, 1964.

Ammonolysis of β-trans-$[\phi PNCl]_4$ when carried out in chloroform or benzene results in the formation of two products, β-trans and α-trans-$[\phi PNNH_2]_4$. However, the same reaction when carried out in tetrahydrofuran gives only β-trans-$[\phi PNNH_2]_4$.[1] The reaction of β-trans-$[\phi PNCl]_4$ with ammonia in THF was run four times and, in each case, the yield of β-trans tetrakisamide exceeded 75%. Results of these runs are summarized in Table I.

Thermal deammoniations of the β-trans tetrakisamide have been carried out at 260°C. in the absence of solvent.[3] The degree of polymerization was not studied as a function of temperature, however, this is now being done.

TABLE I.

Synthesis of β-trans-$[\phi PNNH_2]_4$

Starting $[\phi PNCl]_4$		$[\phi PNNH_2]_4$			Residue	
Weight	m.p.	Weight	m.p.	% Yield	Weight	m.p.
3.0 g.	234-8°C.	2.75 g.	224-5°	92	-	-
49.0	234-8	8.3	222-4	78	5.2	< 215
		19.0	221-2			
		8.2	220-3			
50.1	234-8	18.3	222-3	75	6.5	214-7
		9.1	219		2.5	< 210
		6.0	221-2			
51.0	234-8	17.8	223-4	86	6.5	< 210
		9.8	221-2			
		10.8	219-20			

Tetrakisamide was observed to eliminate ammonia at 200°C., which is below its melting point of 224°. Polymerization of 3 g. samples were carried out at 209°, 218° and 230°. In each case over 90% of the available ammonia was eliminated, i.e., for each two NH_2 groups one NH_3 is eliminated. The resultant polymers were then washed with chloroform and molecular weights determined for the soluble fraction. Thermal polymerization data are summarized in Table II.

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3. NASw-924, Quarterly Report No. 5

TABLE II

Thermal Polymerization of β-trans-$[\phi PNNH_2]_4$

Exp. No.	Temp., °C	Physical State	% NH_3 Elim.	% Sol. in $CHCl_3$	M.W.*
4046-32	209± 1	Solid	91.6	37.2	1,050
4046-33	218± 4	Solid Melt at 24% NH_3 elim.	96.4	70.7	2,800
4046-36A	230± 1	Melt	96.4	33.6	Not Determ.
4046-36B	230± 1	Melt	100.0	37.4	2,000

* Molecular weights determined by VPO in $CHCl_3$.

The soluble polymers are now being fractionated by partial precipitation from chloroform/n-hexane. However, it appears that, from the data collected in Table II, the molecular weight of the soluble polymer prepared by deammoniation in the solid phase is low, principally that of a dimer, whereas those polymerizations carried out in the melt resulted in somewhat higher molecular weight soluble polymers.

III. Preparation of Octaphenoxyphosphonitrilic Cyclic Tetramer

The compound $[(\phi O)_2PN]_4$ was prepared in order to study the stability of the P-Oϕ bond. Hexaphenoxyphosphonitrile trimer has been reported to be quite stable and that it is distillable at 500°C.[4]

The octaphenoxy tetramer was prepared by treating $[PNCl_2]_4$ with excess sodium phenoxide in refluxing toluene for forty eight hours. A yield of 40%, after recrystallization, was obtained. The melting point of the product is 69.5-70°C. and the infrared spectrum is shown in Figure 2. Elemental analysis was:

	C	H	N	P
Calcd. for $C_{12}H_{10}O_2PN$:	62.4	4.3	6.1	13.4
Found :	62.2	4.4	6.2	13.7

4. Inorganic Polymer Symposium, London, Ontario, 1963.

EXPERIMENTAL

I. Preparation of $[CH_3PN(NH_2)]_{3,4}$.

A mixture of 0.40 moles of freshly prepared CH_3PCl_4 and 4.0 moles of freshly prepared NH_4Cl (from NH_3 and HCl) was heated at 132°C. in 500 ml. of chlorobenzene for sixteen hours. Hydrogen chloride evolution was 92% of the theoretical amount expected. Approximately a 100% excess of gaseous ammonia was passed through the solution. The heavy precipitate that resulted contained NH_4Cl and the phosphonitrilamide. The mixture was extracted over night with acetonitrile. From the acetonitrile was recovered 8.7 g. of impure $[CH_3PN(NH_2)]_{3,4}$.

Thermal degradation of the product was carried out initially on an Aminco thermogravimetric balance using a nitrogen sweep at heating rate of 3°/min.. The TGA curve is reproduced in Figure 3.

II. Preparation of β-trans-$[\phi PNCl]_4$

β-trans-$[\phi PNCl]_4$ was synthesized by reacting ϕPCl_4, prepared from ϕPCl_2 and Cl_2, with NH_4Cl in the absence of solvent. A 200% excess of NH_4Cl was used. The mixture was maintained at about 180°C. until no further HCl evolution was observed. The mixture was washed with benzene to separate phosphonitrile from unreacted NH_4Cl. Cyclic tetramer was recovered by a series of fractional crystallizations from benzene.

III. Preparation of β-trans-$[\phi PNNH_2]_4$

Fifty grams of β-trans-$[\phi PNCl]_4$ were put into 300 ml. of THF. Not all of the tetrachloro compound dissolved. Ammonia gas was passed through the solution at room temperature. After several hours the solution was filtered to remove ammonium chloride. More ammonia was added to the filtrate but no precipitate was observed. The reaction therefore was assumed to be completed. Tetrakisamide was recovered by considerably reducing the volume of solution at reflux, and allowing a precipitate to form while cooling.

The reaction was repeated four times and, in each case, the yield of β-trans-$[\phi PNNH_2]_4$, m.p. 222-4°, exceeded 75%.

IV. Polymerization of β-trans-$[\phi PNNH_2]_4$

A three gram sample of the tetrakisamide in a small reaction flask fitted with a nitrogen purge was heated in an oil bath. The nitrogen purge was passed through water containing Brom thymol blue indicator. Evolution of ammonia was first noted at 200°C.. At 209°C

the ammonia evolution was followed by titrating with standard acid.

Experiments were carried out at 209, 218 and 230°C.. The resultant polymer was then washed with 100 ml. of chloroform and the molecular weight of the soluble polymer determined by VPO in chloroform.

V. Synthesis of $[(\phi O)_2PN]_4$.

In toluene 0.07 mole of $[PNCl_2]_4$ and 0.7 mole of sodium phenoxide was heated at reflux for forty-eight hours. By-product NaCl was removed by filtration and the filtrate was then concentrated until $[(\phi O)_2PN]_4$ precipitated. The solid was recrystallized from benzene and 15.3 g. of product (40% yield) was obtained, m.p. 69.5-70°C..

MANPOWER EXPENDED

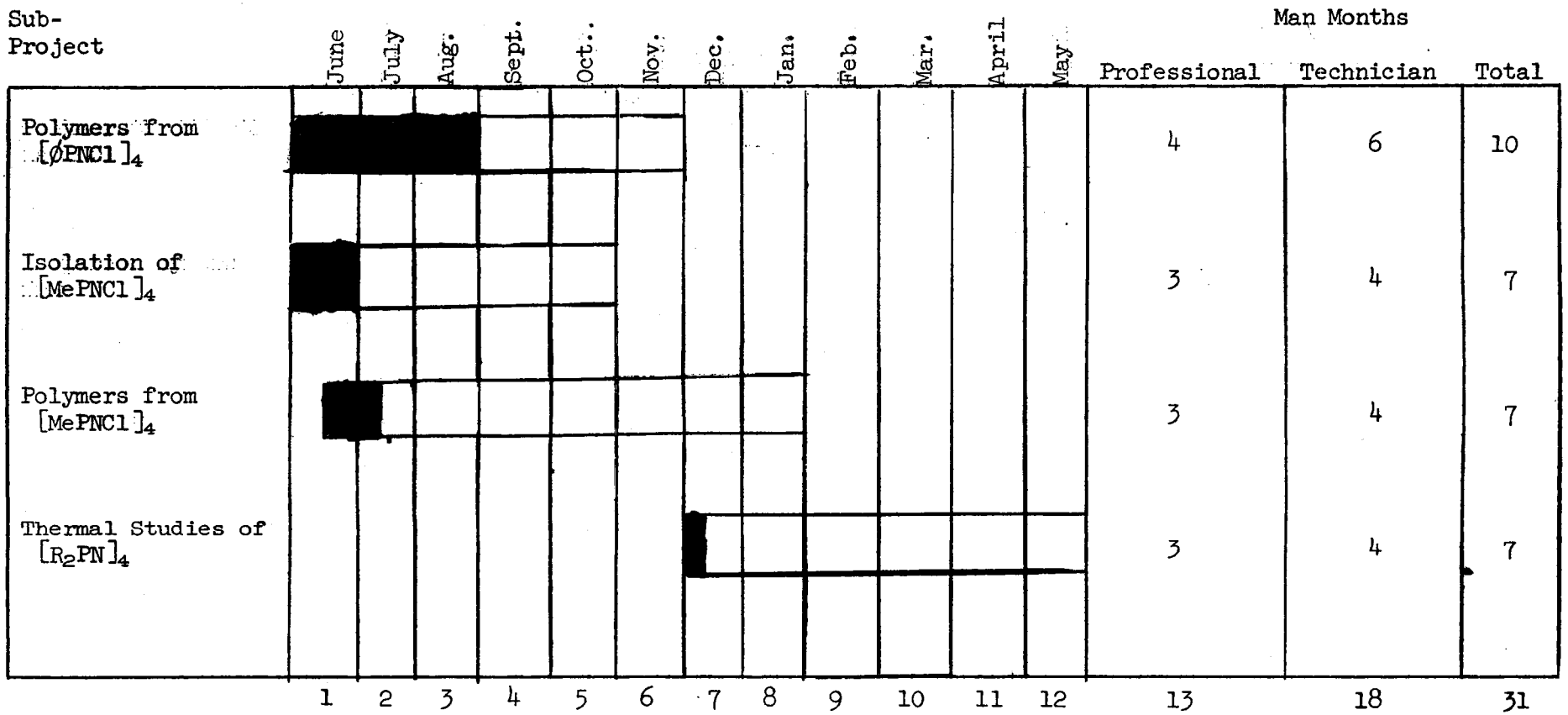
The following breakdown shows the cumulative man hours expended to date:

	Through		
	June	July	August
Principal Investigator	30	39	61
Department Director	8	8	14
Senior Chemist	39	107	213
Technician	360	640	992
Analytical Chemist	0	0	2
Analytical Technician	0	0	2

PROGRAM PLANNING CHART

Attached is the current planning chart. Dark areas represent work accomplished.

DURATION OF SUBPROJECT



ANTICIPATED WORK

Continue polymerization studies of β-trans-$[\emptyset PNNH_2]_4$ by deammoniation reactions at various temperatures.

Investigate other polymerization reactions of β-trans-$[\emptyset PNCl]_4$.

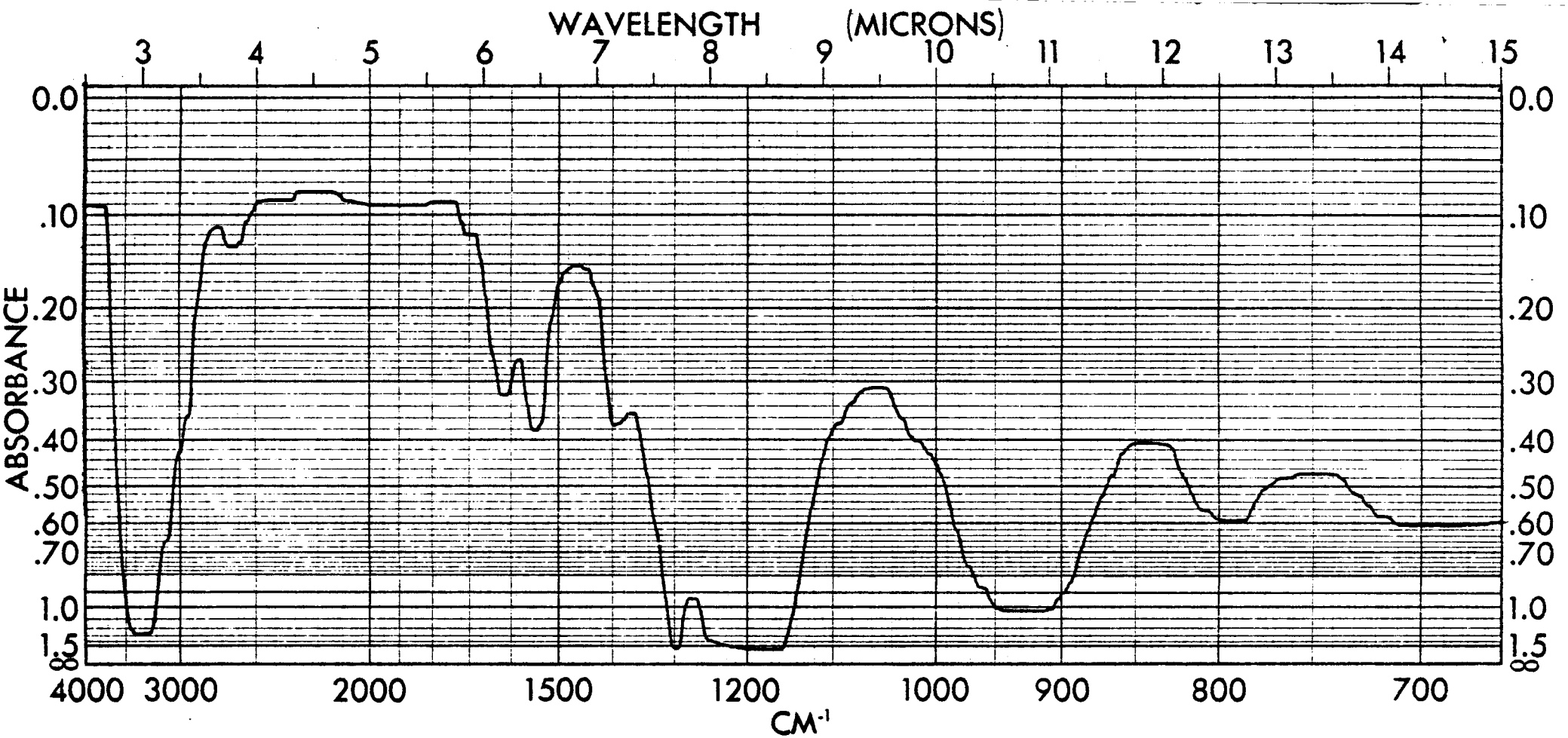


FIGURE 1

Impure $[MePN(NH_2)]_{3,4}$
Extracted from NH_4Cl with CH_3CN

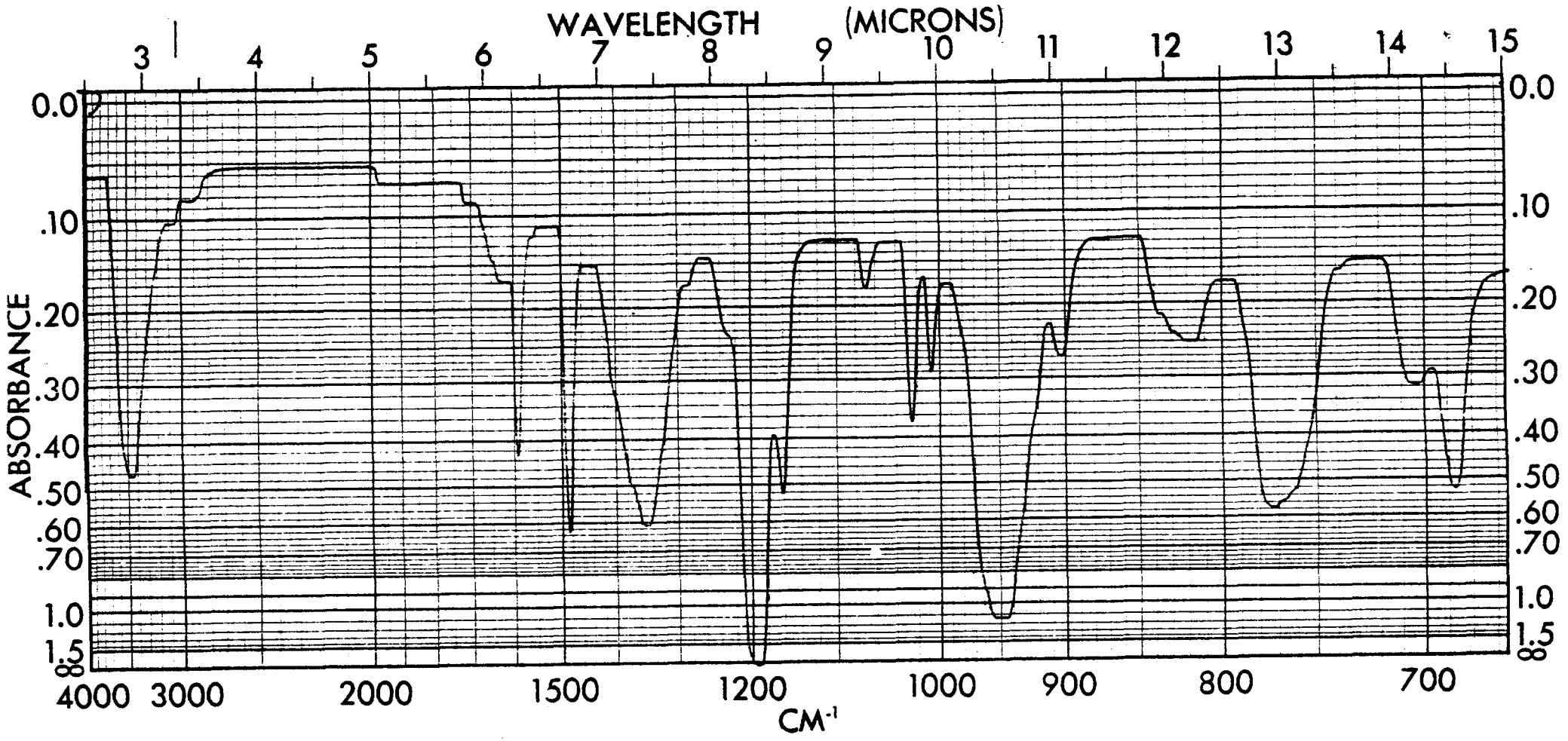


FIGURE 2

$[(C_6H_5O)_2PN]_4$
m.p. 69.5-70

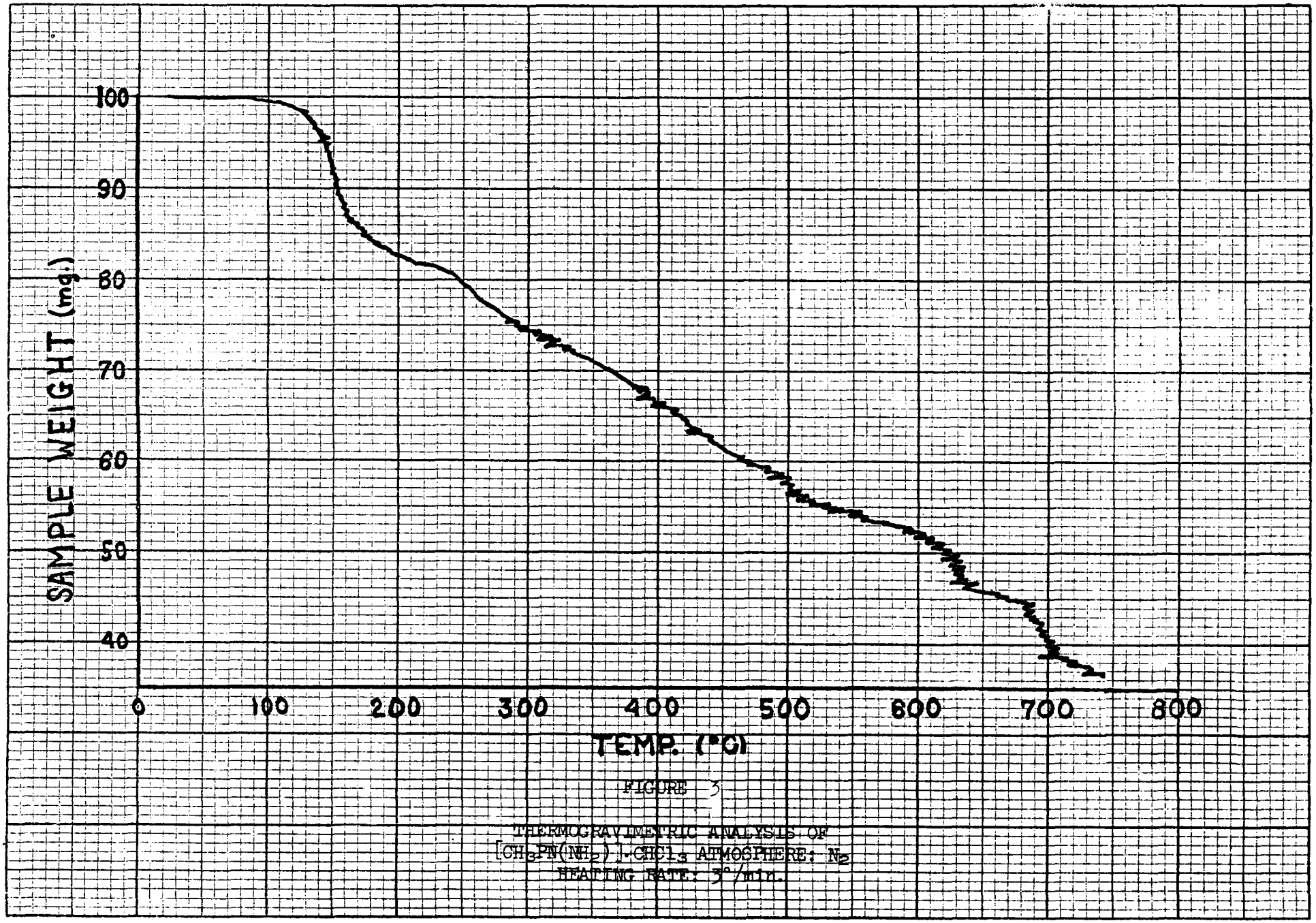


FIGURE 3

THERMOGRAVIMETRIC ANALYSIS OF $[CH_3PN(NH_2)]_3 \cdot CHCl_3$ ATMOSPHERE: N_2
HEATING RATE: 3°/min.

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